CC=JP DATE=20020319 KIND=KOKAI PN=200279600

ANTIREFLECTION LAMINATE
[HANSHA BOUSHI SEKISOUTAI]

TOSHIAKI YOSHIHARA, ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE WASHINGTON, D.C. SEPTEMBER 2009
TRANSLATED BY: SCHREIBER TRANSLATION, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	200279600
DOCUMENT KIND	(12):	KOKAI
PUBLICATION DATE	(43):	20020319
APPLICATION NUMBER	(21):	2000268173
APPLICATION DATE	(22):	20000905
INTERNATIONAL CLASSIFICATION	(51):	B 32 B 7/02 27/30
		C 09 J 7/04 C 09 D 4/02 5/00
PRIORITY COUNTRY	(33):	
PRIORITY NUMBER	(31):	
PRIORITY DATE	(32):	
INVENTOR (S)	(72):	Toshiaki Yoshihara Toru Okubo Koichi Ohata
APPLICANT(S)	(71):	Toppan Printing Co., Ltd.
DESIGNATED CONTRACTING STATES	(81):	
TITLE	(54):	Antireflective Laminate
FOREIGN TITLE	[54A]:	Hansha boushi sekisoutai

[Scope of Claims]

[Claim 1] An antireflective laminate with a low-refraction composition coating having a nanoporous structure formed on at least one surface of a substrate consisting of glass, plastic, or the like; which antireflective laminate is characterized in that the haze of the aforementioned low-refraction composition coating is 1 % or less, the tenpoint average roughness Rz of a micro region 5 μ m square is 100 nm or less, and the arithmetic average roughness Ra is 2 \sim 10 nm

[Claim 2] The antireflective laminate according to Claim 1, characterized in that the main components of the aforementioned low-refraction composition coating are ultrafine inorganic particles having an average particle diameter of $5 \sim 100$ nm and an acrylic compound having in its molecule at least three polymerizable unsaturated bonds, such as vinyl groups, acryloyl groups, or methacryloyl groups.

[Claim 3] The antireflective laminate according to Claim 1 characterized in that the aforementioned low-refraction composition coating contains, in addition to the components of the aforementioned low-refraction composition coating set forth in Claim 2, an organic silicon compound

represented by

General Formula (A) R' Si(OR)4-v

(R: alkyl group; R': functional group having a polymerizable unsaturated terminal bond, such as a vinyl group, an acryloyl group, or a methacryloyl group; x is a substitution number such that 0 < x < 4) and hydrolyzed products thereof.

[Claim 4] The antireflective laminate according to one of Claims 1 \sim 3 characterized in that the aforementioned ultrafine inorganic particles are silica sol particles, 10 % or more of which have a particle diameter in the 50 \sim 100 nm range, and the silica-sol particle content of the low-refraction composition coating is 40 \sim 80 %.

[Claim 5] The antireflective laminate according to one of Claims 1 \sim 4 characterized in that the aforementioned acrylic compound comprises a trifunctional or a higher-functional acrylic monomer and modified products thereof and has an average molecular weight of 200 \sim 1000. [Claim 6] The antireflective laminate according to one of

Claims 1 ~ 5 characterized in that the aforementioned organic silicon compound is an acryloyl group-containing silicon compound represented by

General Formula (B) $CH_2 = CHCOO - (CH)_n - Si(OR)_4$ (R: alkyl group; x is a substitution number such that 0 < x

< 4; n is an integer such that n < 5), with which silica sol particles are modified in advance.

[Claim 7] The antireflective laminate according to one of Claims 1 \sim 6 characterized in that the surface of silica sol particles is modified with the aforementioned acryloyl group-containing silicon compound in such a manner that the molar ratio of the silica sol particles to the acryloyl group-containing silicon compound falls within the range of $1/0.04 \sim 1/0.25$ (weight equivalent of $90/10 \sim 60/40$ wt %).

[Detailed Description of the Invention]

[Technical Field of the Invention] The present invention relates to antireflective laminates, which antireflective laminates have an optical multilayer film formed by coating a transparent substrate, such as glass or plastic.

[Prior Art] A conventionally known method of forming an optical interference multi-layer film, such as an antireflective film, involves the formation of a thin film of an organic oxide, such as titanium oxide or a silicon oxide, on a glass, plastic, or a similar substrate by vapor deposition, sputtering, or another dry coating method.

However, the method entails such problems as that the

devices required for the dry coating processes are expensive and that the productivity is low due to the slow film formation speed. As opposed to this, a method of forming an optical multilayer film by coating a substrate with a metal alkoxide or the like as a starting composition is known. A method has been proposed wherein an alkoxide of a metal, such as Ti or Zr, is used as a high-refraction material, while a silicon alkoxide or a so called silane coupling agent, which is an organic silicon compound having a part of the silicon alkoxides substituted with another organic substituent group (e.g., an epoxy group or an alkyl group), is used as a low refraction material. However, there was a problem with the coating films in terms of productivity, since high temperatures and long time are required for heat curing. Further, while it was possible, to a certain extent, to obtain a low refractive index, there was the flaw that they cannot withstand actual use due to inadequate physical strength, including hardness, abrasion resistance, and adhesion to the substrate. [0003] Proposals have been made to improve on the foregoing, including, for example, complex materials comprising silica sol having a silicon alkoxide as a starting substance and a reactive organic silicon compound (e.g., silane coupling agents, dimethyl silicon having a

terminal reactive group) disclosed in Unexamined Patent Publication No. 09-220791.

[0004]

[Problems to Be Solved by the Invention] However, a long time is also required for heating in the case of these silicon oxide (SiO2)-based complex compositions in order to obtain the desired properties. While organic silicon compounds containing an acryloyl group or another polymerizable unsaturated group are also listed, they are all monofunctional or bifunctional compounds having one or two acryloyl groups and do not yield a high crosslink density, even when photopolymerized (including electron beam (EB) photopolymerization). Attempts to enhance their physical strength, such as hardness and abrasion resistance, require combining a component other than the silica components (e.g., an acrylic compound) into the aforementioned complex film components to increase the acrylic component ratio. This results in a decrease in the volume ratio of the silicon component having a silicon alkoxide or another alkoxide as a starting substance, which component determines the optical properties, leading to the disadvantage of being unable to achieve a low refractive index. A composition heretofore has not been found that yields an optical multilayer film having both a low

refractive index and adequate physical properties, including hardness, abrasion resistance, and adhesion to the substrate.

[0005] The present invention was made in view of the foregoing problems for the purpose of providing an antireflective laminate that has a low refractive index, excels in physical strength, including hardness, abrasion resistance, and adhesion to the substrate, is inexpensive, and excels in productivity.

/3

[0006]

[Means for Solving the Problem] In order to solve the foregoing problems, the invention according to Claim 1 is an antireflective laminate with a low-refraction composition coating having a nanoporous structure formed on at least one surface of a substrate consisting of glass, plastic, or the like; which antireflective laminate is characterized in that the haze of the aforementioned low-refraction composition coating is 1 % or less, the tenpoint average roughness Rz of a micro region 5 μ m square is 100 nm or less, and the arithmetic average roughness Ra is 2 ~ 10 nm.

[0007] The invention according to Claim 2 is an antireflective laminate according to Claim 1, characterized

in that the main components of the aforementioned lowrefraction composition coating are ultrafine inorganic
particles having an average particle diameter of 5 ~ 100 nm
and an acrylic compound having in its molecule at least
three polymerizable unsaturated bonds, such as vinyl
groups, acryloyl groups, or methacryloyl groups.
[0008] The invention according to Claim 3 is an
antireflective laminate according to Claim 1 characterized
in that the aforementioned low-refraction composition
coating contains, in addition to the components of the
aforementioned low-refraction composition coating set forth
in Claim 2, an organic silicon compound represented by

General Formula (A) R'x Si(OR)4-x

(R: alkyl group; R': functional group having a polymerizable unsaturated terminal bond, such as a vinyl group, an acryloyl group, or a methacryloyl group; x is a substitution number such that 0 < x < 4) and hydrolyzed products thereof.

[0009] The invention according to Claim 4 is an antireflective laminate according to one of Claims 1 ~ 3 characterized in that the aforementioned ultrafine inorganic particles are silica sol particles, 10 % or more of which have a particle diameter in the 50 ~ 100 nm range, and the silica-sol particle content of the low-refraction

composition coating is 40 ~ 80 %.

[0010] The invention according to Claim 5 is an antireflective laminate according to one of Claims $1 \sim 4$ characterized in that the aforementioned acrylic compound comprises a trifunctional or a higher-functional acrylic monomer and modified products thereof and has an average molecular weight of 200 \sim 1000.

[0011] The invention according to Claim 6 is an antireflective laminate according to one of Claims 1 \sim 5 characterized in that the aforementioned organic silicon compound is an acryloyl group-containing silicon compound represented by

General Formula (B) $CH_2 = CHCOO - (CH)_n - Si(OR)_4$ (R: alkyl group; x is a substitution number such that 0 < x < 4; n is an integer such that n < 5), with which silica sol particles are modified in advance.

[0012] The invention according to Claim 7 is an antireflective laminate according to one of Claims 1 \sim 6 characterized in that the surface of silica sol particles are modified with the aforementioned acryloyl groupcontaining silicon compound in such a manner that the molar ratio of the silica sol particles to the acryloyl groupcontaining silicon compound falls within the range of $1/0.04 \sim 1/0.25$ (weight equivalent of $90/10 \sim 60/40$ wt %).

[0013] <Technical Functions> According to the present invention, by forming a low-refraction composition coating comprising inorganic particles and a binder so that the surface roughness thereof is such that the ten-point average roughness Rz of a 5 µm square micro region is 100 nm or less and the arithmetic average roughness Ra is 2 ~ 10 nm, it is possible to form a low-refraction laver with a nanoporous structure having a delicate asperity of a nano order while maintaining transparency (low haze value) without the impact of light scattering; and, by forming a nanoporous structure having asperity of a nano order, air pores are introduced into the coating film, and the apparent refractive index is thus lowered. [0014] By comprising the low-refraction composition mainly of silica sol particles and a multifunctional acrylic compound having multiple polymerizable unsaturated terminal bonds, such as vinyl, acryloyl, or methacryloyl groups, the coating film is cured after formation by irradiating with ultraviolet rays (UV) or electron beams (EB) to cause the acryloyl and/or other polymerizable unsaturated groups in the coating film to crosslink through photopolymerization. It is possible to form a suitable nanoporous structure by controlling the diameter of silica sol particles and the

ratio of multifunctional acrylic compound, which is the

binder. While the composition itself functions as a lowrefraction component, the nanoporous structure renders it possible to achieve a low refractive index (1.40 or less) that cannot be achieved based on the refractive index of the materials (refractive index of silica - about 1.45; refractive index of the acrylic component - about 1.50). [0015] Physical strength, such as hardness and abrasion resistance, is normally determined by the quantity of acryl groups and the like introduced. These acryl group components normally have a refractive index slightly higher than that of the silicon components. Thus, while an increase in acrylic components results in improved strength, it results in an increase in the refractive index. By using certain multifunctional acrylic compounds, the low-refraction composition according to the present invention exhibits strength even with a small quantity of binder. In particular, by using trifunctional or higherfunctional acrylic monomers, such as dipentaerythritol hexaacrylate (DPHA), instead of a prepolymer having a large molecular weight, it is possible to form a more even hybrid film with a higher crosslinking density. Additionally, by forming a complex (modifying the particles) with an acryloyl group-containing organic silicon compound, it is possible to further enhance the crosslinking density of the coating film. It exhibits adequate strength even with a nanoporous structure, since it has a uniform hybrid structure on the molecular level, resulting in a large volume ratio of low-refraction components, such as silica sol. Thus, it is hard, excels in abrasion resistance, renders possible significant improvement as regards disadvantages found in antireflective laminates comprised of convention low-refraction compositions, and provides an antireflective laminate that has both a low refractive index and high strength.

/4

[0016]

[Embodiments of the Invention] An embodiment of the present invention is described in detail hereafter. An antireflective laminate according to the present invention is an antireflective laminate with a low-refraction composition coating having a nanoporous structure formed on at least one surface of a substrate consisting of glass, plastic, or the like; which antireflective laminate is characterized in that the haze of the aforementioned low-refraction composition coating is 1 % or less, the tenpoint average roughness Rz of a micro region 5 µm square is 100 nm or less, and the arithmetic average roughness Ra is

[0017] The arithmetic average roughness Ra and the tenpoint average roughness Rz in the present invention was calculated in compliance with the definition set forth in JIS-B0601. It signifies the surface roughness of a micro region measured on a nano scale using an atomic force microscope or the like. Since the antireflective laminate according to the present invention is an antireflective layer that employs optical interference in the visible region, the coating film layered needs to be generally 100 nm ~ 200 nm in thickness, be a continuous film, and have a surface roughness that will not impact light scattering. Since excessively large variance in or frequent occurrence of asperity leads to an increase in the haze of the coating film and a decline in strength, Rz of 100 nm or less and Ra within the 2 ~ 10 nm range are preferred.

[0018] An antireflective laminate according to the present invention is characterized in that the aforementioned low-refraction composition coating are ultrafine inorganic particles having an average particle diameter of $5 \sim 100$ nm and an acrylic compound having in its molecule at least three polymerizable unsaturated bonds, such as vinyl groups, acryloyl groups, or methacryloyl groups; 10 % or more of the aforementioned ultrafine inorganic particles have a diameter in the $50 \sim 100$ nm range; and the silica-

sol particle content of the low-refraction composition coating is 40 ~ 80 %. The low-fraction composition is comprised of ultrafine inorganic particles and a binder; examples of the ultrafine inorganic particles are lowfraction particles, such as fluorides (e.g., MgF2) and silicon oxide, and examples of binders are melamine resins and urethane resins. However, an antireflective laminate according to the present invention requires abrasion resistance and other types of strength, since it is normally applied onto and used on the outermost layer of a display device, such as an LCD, and specific low-fraction compositions are required in order to solve these problems. [0019] Silica sol particles used in the present invention are silica particles having a diameter such that the average particle diameter is 5 ~ 100 nm and dispersed in a solvent; which silica sol is obtained by removing the alkali, by ion exchange or another method, from or by neutralizing an alkaline silicate, such as sodium silicate. While there are no limitations on whether the silica sol thus obtained is aqueous or organic solvent-substituted and organic solvent-based, organic solvent-based silica sol is preferred in terms of compatibility with acrylic monomers and coatability of plastic substrates. It is difficult to produce those of 5 nm or smaller, and transparency is

impaired due to light scattering if 100 nm or larger. The ratios of the particles and the binder are important for the achievement of a nanoporous structure, and the total silica particle content of the low-refraction composition coating film according to the present invention is preferably 30 ~ 80 wt% and more preferably 40 ~ 70 wt%. It is difficult to achieve the desired refractive index at 30 % or less, and adequate strength cannot be achieved at 80 % or higher. In particular, an optimum nanoporous structure can be achieved by having 10 wt% or higher, and more preferably 20 wt% or higher, of large particle content comprising particles having a particle diameter of 50 ~ 100 nm. There is little effect thereof at 10 wt% or lower. [0020] A multifunctional acrylic compound used in the present invention has at least three polymerizable unsaturated bonds in its molecule, such as vinyl, acryloyl, and/or methacryloyl groups; and examples thereof include acrylic monomers, such as dipentaerythritol hexaacrylate (DPHA), as well as the modified products and derivatives thereof. In particular, DPHA, pentaerythritol acrylate (PETA), or multifunctional acrylic monomers, such as prepolymers produced by reacting PETA with a diisocyanate, such as hexamethylene diisocyanate (HDI), and their modified products having a molecular weight of 200 ~ 1000

are satisfactorily compatible with silica sol and can form, without phase separation, an even and transparent hybrid coating film with a high crosslinking density.

[0021] Further, an antireflective laminate according to the present invention is characterized in that the aforementioned low-refraction composition coating contains an organic silicon compound represented by

General Formula (A) R'x Si(OR)4-x

(R: alkyl group; R': functional group having a polymerizable unsaturated terminal bond, such as a vinyl group, an acryloyl group, or a methacryloyl group; x is a substitution number such that 0 < x < 4) and hydrolyzed products thereof. Examples of acryloyl group-containing organic silicon compounds include vinyl trimethoxy titanium, methacryloxy tri-isopropoxy titanate, and methacryloxy propryl tri-isopropoxy zirconate. Preferred in particular are acryloyl containing silicon compounds represented by

General Formula (B) $CH_2 = CHCOO - (CH)_n - Si(OR)_4$ (R: alkyl group; x is a substitution number such that 0 < x < 4; n is an integer such that n < 5), a typical example of which is (3-acryloxypropyl)trimethoxy silane. These organometallic silicon compounds may be caused to form a coating film through a hydrolysis reaction following

coating using atmospheric moisture by adding an organic acid catalyst, such as p-toluenesulfonic acid, to the composition, or it is possible to add water (including a catalyst, such as hydrochloric acid) in advance and use the hydrolysis reaction products thereof. At this time, it is possible to obtain a stable composition by using hydrolysis products obtained by hydrolyzing the organic silicon compound using a quantity of water equal to 1/8 ~ 7/8 of the

quantity of water necessary for the hydrolysis of all alkoxyl groups in said organic silicon compound, and it is possible to use them without excess water remaining or the need for special separation and refinement.

[0022] In the preparation of the aforementioned hydrolyzed products of organic silicon compounds, phase separation is inhibited by suppressing the growth of silicon compound polymers and enhancing compatibility by suppressing the side reaction of acrylic compounds with excess water and controlling the hydrolysis rate of the silicon compounds, thus causing the formation of a molecular-level hybrid film that is even and has a high crosslinking density. Although combinations of such hybrid compositions are generally known to the public, the composition according to the present invention is not merely a combination, but is a

material system with high compatibility and affinity between the inorganic network of the coating composition, which is a matrix, and the inorganic filler. The system yields a better dispersion state than a mere dispersion in an organic resin, a coating film with high adhesion between the filler and the matrix, and greater effect than regular addition effect. In particular, when silica sol particles and an organic silicon compound represented by General Formula (A) are mixed and reacted in advance in a different system to modify the particle surface when modifying particles of an acryloyl group-containing silicon compound, as it enhances the effect of yielding adequate strength even with a reduced quantity of the acrylic compound, which serves as the binder component, and results in a nanoporous structure preferable for the compositions of an antireflective laminate according to the present invention. [0023] Further, the aforementioned method of modifying the particle surface is such that the treatment can be performed easily by causing the alkoxide group of an organic metal and the OH group on the particle surface to react, and it is possible to prepare the coating composition by adding the other components as is without specifically preparing the composition separately. Particularly when modifying particles of an acryloyl groupcontaining silicon compound, the reaction is preferably caused to take place in an organic solvent, such as an alcohol or a ketone system, in the presence of a sulfonic acid catalyst, such as p-toluenesulfonic acid, to achieve satisfactory modification efficiency and prevent water from mingling with the solvent.

[0024] Further, the molar ratio of the silica sol particles to the acryloyl group-containing silicon compound preferably falls within the range of 1/0.04 ~ 1/0.25 (weight equivalent of 90/10 ~ 60/40 wt %) to enable the achievement of both a nanoporous structure and strength. In the present invention, a nanoporous structure signifies pores that are so microscopic that they are not impacted by light scattering, and there is no particular limitation on whether the pores are closed or open. While the aforementioned pores are of a certain size physically, they are often microscopic and irregular in shape, and often cannot be observed directly by electron microscopes or the like. Should that be the case, the refractive index was measured by optical means and a nanoporous was presumed to be present if a phenomenon that deviates from the additive property of multi-component system was observed. For example, when silica particles having a refractive index of 1.45 and an acrylic binder having a refractive index of

1.52 are used, a 50/50 vol% mixture is generally observed to have a virtually mean refractive index of 1.47 ~ 1.49. In the case of a nanoporous structure according to the present invention, a phenomenon of significant deviation from the additive property can be observed, the apparent refractive index being lower than the foregoing at 1.45 or lower or, depending on particle diameters, 1.35 or lower. It is inferred from these phenomenon that the coating film has a nanoporous structure; that is, it is presumed that the apparent refractive index is reduced due to the presence of microscopic pores. The low-refraction compositions according to the present invention were also defined as having a nanoporous structure by measuring the refractive indices of compositions with varying binder ratios using refractometry, and there is no particular limitation on the configuration of the nanoporous structure or the distribution in the film-thickness direction (for example, the structure is tilted towards the surface direction). [0025] When curing by UV ray irradiation, a radical polymerization initiator is preferably added. There is no particular limitation thereon, and examples include benzoin ether-based initiators, such as benzoin methyl ether; acetophenone-based initiators, such as acetophenone and 2.1-hydroxycyclohexyl phenyl ketone; and benzophenone-based

initiators, such as benzophenone.

[0026] Combinations of a number of the components described above may be added to the coating composition, and dispersants, stabilizers, viscosity modifiers, colorants, and other known additives may be further added to the extent that they do not impair the properties thereof. [0027] Because an antireflective laminate according to the present invention is installed on the outermost layer, it is required to have the so-called antifouling property, such as the prevention of surface contamination and ease of wiping off fingerprints and other grime. In such a case, it is possible to add the so-called antifoulants, examples of which include fluorine-containing acrylic compounds and silicon-based additives. Among them, fluorine-containing acrylic compounds and fluorine-containing silane coupling agents are preferred due to their reactivity with the coating film components.

[0028] Conventionally known means, such as the dipping method, roll coating method, screen printing method, and spraying method, are used as application methods for the coating composition. The thickness of the coating film can be selected and adjusted suitably depending on the intended optical design, the concentration of the liquid, and the coating quantity.

[0029] Lamination with the low-refraction compositions according to the present invention is not particularly limited to glass, plastic films, and the like, and it is possible to further layer them with various hard coating agents, high-refraction materials, low-refraction materials, and vapor-deposited ceramic layers as necessary, as well as layer them in varying composition ratios as needed.

[00301

[Working Examples] Antireflective laminates according to the present invention are described with references to concrete working examples.

[0031] <Working Example 1> A triacetyl cellulose (TAC) film that is 80 µm in thickness and provided with a hard coating (HC) layer (5 µm) of UV-cured resin was used as the substrate. A solution was prepared by combining the solid components of the coating composition shown below so that

/6

the ratio will be 60 parts by weight of Component B to 40 parts of Component D, and an acetophenone-based initiator was added thereto as an ultraviolet (UV) curing initiator in an amount equal to 2 % of the polymerizing components to obtain a coating composition. The coating composition was applied using a bar coater, dried for 1 minute at 100° C

using a dessicator, and cured by irradiating with 1000 mJ/cm² ultraviolet rays using a high-pressure mercury vapor lamp; and a low-refraction coating film was formed by suitably adjusting the so that the optical film thickness will be nd = 550/4 nm (nd = refractive index n * film thickness d (nm)) to obtain a specimen for testing. The specimen was evaluated in accordance with the evaluation test methods shown below, and the results thereof were indicated in Table 1.

[0032] <Working Example 2> A specimen for testing was obtained in the same manner as in Working Example 1 with the exception of preparing a solution for use as the coating composition by combining components so that the ratios thereof will be 30 parts by weight of Component A, 30 parts by weight of Component B, and 40 parts by weight of Component D, and forming a low-refraction coating film from the coating composition. The specimen was evaluated in the same manner as for Working Example 1, and the results thereof were shown in Table 1.

[0033] <Working Example 3> A specimen for testing was obtained in the same manner as in Working Example 1 with the exception of preparing a solution for use as the coating composition by combining components so that the ratios thereof will be 80 parts by weight of Component C

and 20 parts by weight of Component D, and forming a lowrefraction coating film from the coating composition. The specimen was evaluated in the same manner as for Working Example 1, and the results thereof were shown in Table 1. [0034] <Comparative Example 1> A specimen for testing was obtained in the same manner as in Working Example 1 with the exception of preparing a solution for use as the coating composition by combining components so that the ratios thereof will be 70 parts by weight of Component A and 30 parts by weight of Component D, and forming a lowrefraction coating film from the coating composition. The specimen was evaluated in the same manner as for Working Example 1, and the results thereof were shown in Table 1. [0035] <Comparative Example 2> A specimen for testing was obtained in the same manner as in Working Example 1 with the exception of preparing a solution for use as the coating composition by combining components so that the ratios thereof will be 40 parts by weight of Component D and 60 parts by weight of Component E, and forming a lowrefraction coating film from the coating composition. The specimen was evaluated in the same manner as for Working Example 1, and the results thereof were shown in Table 1. [0036] <Components of the Coating Compositions> (Component A) Silica sol with an average particle diameter of 10 ~ 15 nm / MEK solvent

(Component B) Silica sol with an average particle diameter of $5.0 \sim 70$ nm / MEK solvent

(Component C) A complex sol modified by adding (3-acryloxypropyl)trimethoxy silane to silica sol with an average particle diameter of $50 \sim 70$ nm at a molar ratio of 1/0.08 (weight ratio of approximately 80/20), adding ptoluenesulfonic acid as a catalyst in a quantity equal to 1 wt% of the acrylic silane, and stirring and reacting for three hours at room temperature.

(Component D) Dilute DPHA solution in MEK

(Component E) Silica sol with an average particle diameter of 150 nm / MEK solvent

[0037] <Evaluation Test Methods>

(1) Surface Roughness

It was measured using Atomic Force Microscope AFM (SFI13700: Seiko Electronics) for a 5 µm square scan area.

(2) Optical Reflectance

Reflectance was measured for 550 nm and an incidence angle of 5 using a spectrophotometer.

(3) Haze

The haze was measured in according with JIS-K7105, which is the optical property testing method for plastics.

(4) Adhesion

It was evaluated based on the number of remaining coating film in accordance with the cross-cut adhesion test method in JIS-K5400, which is the coating material general testing method.

(5) Pencil hardness

It was evaluated on the basis of scratches in the coating film in accordance with the pencil scratch value test in JIS-K5400, which is the coating material general testing method.

(6) Abrasion Resistance Test

Abrasion tests were performed by running steel wool #0000 back and forth for a total of 5 times with a load of 250 g/cm² and visually inspecting the external appearance for scratches. They were evaluated on a scale of four: 0 - no scratch, 0 - lightly scratched, \triangle - considerably scratched, \times - prominently scratched.

[0038]

[Table 1]

項目		実施例 1	実施例 2	実施例3	比較例-1	比數例 2
各成分比 (盘量部)	A	-	30	_	70	-
	В	60	30	-	-	-
	c	-		80	-	-
	D	40	40	20	30	40
	B	-	-	-	-	6.0
湊面粗さR z R a	(nm) (nm)	7 0 7	30	6 0 5	10	9 5 1 2
反射率	(%)	1.2	1.5	1.5	2.9	1.3
~1×	(%)	0.7	0,4	0.5	0.3	4.5
磁潜性		100	100	100	100	90
鉛等硬度		2 H	3 H	3 H	н	н
耐擦傷性		0	0	0	Δ	×

/7

Top to bottom, left to right

Item

Component Ratio (parts by weight)

Surface Roughness

Reflectance

Haze

Adhesion

Pencil Hardness

Abrasion Resistance

Working Example 1

Working Example 2

Working Example 3

Comparative Example 1

Comparative Example 2

[0039] As shown in Table 1, the refractive indices of Working Examples 1 ~ 3 are low at 1.5 % or lower. Further, they also excel in terms of strength, including adhesion, hardness, and abrasion resistance. However, in the system of Comparative Example 1, wherein only silica sol with a small average particle diameter was used, the surface was smooth with surface roughness Ra of 1 nm, and the refraction index remained at 1.46 and could not be lowered. In the system of Comparative Example 2, wherein silica sol with a large average particle diameter was used, the coating film clouded over with a haze of 4.5 %, although the refractive index was low. Further, it can be seen that it is also inferior in terms of abrasion resistance.

[Effect of the Invention] As described above, an antireflective laminate according to the present invention

renders possible the provision of an antireflective laminate having both a low refraction index as its optical property and hardness, heat resistance, and the like as its physical properties due to the nanoporous structure achieved through the formation thereof as a coating film having an organic and inorganic compound hybrid structure on the molecular level by forming a low-refraction composition coating film that controls the surface roughness on a nanoscale by applying onto a substrate a low-refraction composition comprising silica sol particles, acrylic group-containing silicon compound, and a multifunctional acrylic monomer. Hence, an antireflective laminate according to the present invention can be formed on the outermost layer of a substrate as the antireflective film for displays and the like, and can sufficiently withstand harsh environments and handling. [0041] Additionally, in comparison with the conventional vapor deposition method and methods wherein an antireflective film is formed from a thin film formed by a dry coating method, such as the sputter method, an antireflective laminate according to the present invention involves relatively low device costs, results in higher productivity, since coating films may be formed at 10 times

or more of the speed conventional methods, and is easy

produce.

[0042] Further, because the low-refraction composition that forms the coating film can be applied at a low temperature since it is cured by optical irradiation, coating can take place at low temperatures. Since it is possible to coat films and the like as they are taken up, there is the effect of enabling mass production for a low cost.